

Influence of Decomposition on Chemical Properties of Plant- and Manure-Derived Dissolved Organic Matter and Sorption to Goethite

James F. Hunt, Tsutomu Ohno,* Zhongqi He, C. Wayne Honeycutt, and D. Bryan Dail

ABSTRACT

Sorption of dissolved organic matter (DOM) plays an important role in maintaining the fertility and quality of soils in agricultural ecosystems. Few studies have examined the effects of decomposition on DOM sorption and chemical characteristics. This study investigated the sorption to goethite (α -FeOOH) of fresh and decomposed hydrophilic (HPL) and hydrophobic (HPB) DOM fractions extracted from the shoots and roots of crimson clover (*Trifolium incarnatum* L.), corn (*Zea mays* L.), soybean [*Glycine max* (L.) Merr.], hairy vetch (*Vicia villosa* L.), and dairy and poultry manures. Sorption was positively related to apparent molecular weight (MW_{AP}), aromaticity as measured by absorptivity at 280 nm, and phenolic acid content. A 10-d laboratory microbial decomposition of the source organic matter generally increased the sorption of the extracted DOM onto goethite. The decomposition effect on sorption was greater for the HPL fractions than for the HPB fractions. There was a decrease in the MW_{AP} values of the DOM samples following sorption to goethite. In many cases the reduction in MW_{AP} was large, indicating a strong preference by goethite for the higher MW_{AP} DOM fractions. The results of this laboratory-based research demonstrate that microbial processes affect the chemical characteristics of DOM which may affect the distribution of soil organic C pools.

THE incorporation of crop residues and animal manures into soils is an important management strategy for maintaining soil quality and nutrient availability through the replenishment of C to the soil ecosystem. Cropping system studies have shown that levels of both total soil organic matter and dissolved organic matter (DOM) are influenced by the type of organic amendment used (Griffin and Porter, 2004; Ohno et al., 2005). In sustainable agricultural practices, which often utilize high inputs of organic matter, the added DOM fraction from fresh or early-stage decomposing soil amendment materials may play an important role in the process of organic matter accumulation. The DOM can influence many chemical processes due to its reactivity with both soil solution components and soil surfaces through a variety of mechanisms such as ligand exchange, hydrophobic interaction, outer sphere binding, or cation bridging (Sposito, 1989).

The chemical properties of DOM have been characterized using many methods. The determination of DOM apparent molecular weight (MW_{AP}) by high performance-size exclusion chromatography with UV-

detection has become a widely used technique (Aoyama, 1996; Hur and Schlautman, 2003). In this method, DOM retention times are converted to MW_{AP} using a calibration curve comprised of known molecular weight standards, and the magnitude of the UV absorbance at each time unit is taken to be proportional to the mass frequency of the associated chromophore (Chin et al., 1994; Zhou et al., 2000). Information about the degree of humification and the aromaticity of DOM has often been assessed using UV absorbance and fluorescence spectroscopic methods. The aromaticity of DOM can be inferred from its molar absorptivity at UV wavelengths of 280 nm or less, as well by the ratio of its UV absorbance at 250 nm to that at 365 nm ($E2/E3$ ratio) (Guo and Chorover, 2003). Acidic functional group contents of DOM, which are involved directly with complexation and ligand exchange reactions (Morel and Hering, 1993), can be determined using potentiometric titrations (Ohno and Cronan, 1997).

Previous studies have found relationships between the biodegradability and the chemical properties of DOM. Increased resistance to biodegradation has generally been found to be associated with low DOM carbohydrate content, as well as with high hydrophobicity and aromatic content (Marschner and Kalbitz, 2003; Kalbitz et al., 2003). Increases in both aromaticity and molecular complexity with biodegradation were reported for forest, fen, and agriculturally derived DOM molecules (Kalbitz et al., 2003). In contrast, a study by Marschner and Bredow (2002) reported that specific UV absorbance did not correlate well with DOM biodegradability, leading the authors to propose that nonaromatic compounds may also vary significantly in biodegradability depending on their degree of polymerization or oxidation.

Studies have shown that organic matter fractionation occurs as a result of the preferential sorption of DOM fractions with greater hydrophobic character, aromatic content, MW_{AP} , and total organic acidity than the DOM that remains in solution (Jardine et al., 1989; Gu et al., 1995; Meier et al., 1999; Kaiser and Guggenberger, 2000; Hur and Schlautman, 2003). Under batch conditions of limited sorption sites, Kaiser and Zech (1997) observed desorption of hydrophilic soil DOM from the surfaces of hydrous metal oxides by hydrophobic soil DOM. Virtually all previous works have focused on the adsorptive fractionation behavior of aquatic or naturally occurring terrestrial humic substances rather than on DOM of particular relevance to agricultural systems. The objec-

J.F. Hunt, T. Ohno, and D.B. Dail, Dep. of Plant, Soil, and Environmental Sciences, Univ. of Maine, 5722 Deering Hall, Orono, ME 04469-5722, U.S.A. Z. He and C.W. Honeycutt, USDA-ARS, New England Plant, Soil, and Water Lab., Orono, ME 04469. Received 5 Apr. 2006. *Corresponding author (ohno@maine.edu).

Published in J. Environ. Qual. 36:135–143 (2007).
Technical Reports: Plant and Environment Interactions
doi:10.2134/jeq2006.0133
© ASA, CSSA, SSSA
677 S. Segoe Rd., Madison, WI 53711 USA

Abbreviations: C_{TS} , total soluble carbon; DI- H_2O , deionized distilled water; DOM, dissolved organic matter; HPB, hydrophobic; HPL, hydrophilic; ICP-AES, inductively coupled plasma-atomic emission spectrometry; MW_{AP} , apparent molecular weight.

tives of this study were to examine: (1) the chemical characteristics of water-extractable DOM from fresh and decomposed crop shoots, crop roots, and animal manures; and (2) the sorption of these DOM molecules onto goethite. An XAD-based procedure was used to separate the hydrophilic (HPL) and hydrophobic (HPB) fractions of the water-extractable DOM to gain additional insight into the role of each operational fraction in the sorption process.

MATERIALS AND METHODS

Aqueous Extracts

Plant shoot biomass was obtained from field-grown corn (*Zea mays* L.), soybean (*Glycine max* L. Merr.), crimson clover (*Trifolium incarnatum* L.), and hairy vetch (*Vicia villosa* L.). Root biomass was obtained from 3-wk-old hydroponically grown plants of these crop species. All shoot tissues were air-dried and ground before passing through a 1-mm sieve. Plant root tissues were air-dried and used unsieved. The locally obtained dairy and poultry manure samples were air-dried and passed through a 2-mm sieve. The fresh DOM from these materials was obtained by extracting the materials at a 40:1 (v/w) water to residue ratio using cold deionized distilled water (DI-H₂O) and refrigerating (4°C) the mixtures for 18 h with periodic hand shaking. Suspensions were then centrifuged (900 × g) for 30 min before vacuum-filtering through 0.4-μm polycarbonate filters.

Decomposition

Decomposition incubations were performed by using a procedure modified from that used by Merritt and Erich (2003). Briefly, 2 g of plant biomass or manure sample and 10 mL of DI-H₂O were added to 36 g of acid-washed silica sand in 125-mL polyethylene screw-top bottles. Thirty μL of a fresh field soil extract (1:10, soil/DI-H₂O) was added to each bottle to provide a microbial population representative of field soils for the decomposition process. Carbon/N ratios were determined for the plant and manure samples using a LECO CN-2000 carbon-nitrogen analyzer and ammonium nitrate was added as necessary to attain a C/N ratio of 20 for each sample before incubation. The bottles were shaken, loosely capped, and placed in the dark at room temperature. Bottles were weighed on alternate days and remoistened with DI-H₂O as necessary to maintain the initial moisture level. The decomposed DOM was extracted on Day 10 in the same manner as for the fresh samples. Three replicates of each material and a control consisting of sand, inoculant, and DI-H₂O were analyzed.

XAD Fractionation

The HPL and HPB fractions of both fresh and decomposed DOM extract for each material were obtained by passing the filtered extracts through 20 to 60 mesh XAD-7 (Rohm and Haas; Philadelphia, PA) resin columns. The XAD-7 resin was used in place of XAD-8 in this study because of its greater surface area, smaller average pore diameter, and lower tendency to bleed at high DOC loading (Zhaoyi et al., 1997; Gadmar et al., 2005). Both resins are acrylic esters of moderate polarity and would be expected to fractionate materials in a similar manner. The XAD-7 resin was prepared with three 50-mL rinses of 0.1 M NaOH and DI-H₂O, followed by Soxhlet extraction with methanol for 3 h. Ten mL of the resin was then added to a column and rinsed sequentially with 100 mL each of DI-H₂O, 0.01 M NaOH, and 0.01 M HCl (Ohno and Cronan,

1997). The DOM solutions were acidified to pH 3 using dropwise additions of 1 M HCl and passed through the XAD-7 columns at a rate of 2 mL min⁻¹. The eluent was defined as the HPL fraction and the HPB fraction was taken to be that which desorbed from the resin with 0.1 M NaOH. The concentrations of total soluble organic carbon (C_{TS}) in each of the fractions were determined using a Shimadzu 5000 Carbon Analyzer. Except for an aliquot that was used for potentiometric titration (see below), each solution was then diluted to 5 mM C_{TS} and neutralized to pH 7 before further testing.

Dissolved Organic Matter Characterization

Carboxyl and phenolic acidity were determined by potentiometric titration in a glass reaction beaker maintained at 25.0 ± 0.1°C. The extracts were passed through a proton-saturated cation exchange resin before dilution to 20 mM C_{TS}, pH 3, and ionic strength of 20 mM with dilute NaOH and 1 M KCl. Nitrogen was bubbled through the solutions for 15 min before titration to minimize CO₂ contamination, and the resultant solutions were titrated with standardized 0.05 M NaOH. The moles of OH⁻ consumed between the operational beginning and end points of pH 3 and pH 7 were taken to be equal to the carboxyl acidity of the DOM. The phenolic acidity of the DOM was estimated as the number of moles of OH⁻ consumed between pH 7 and pH 10. Due to the wide variations in pK_a values possible for substituted phenols, this approximation may have underestimated phenolic acidity. Blank corrections were made by subtracting the quantity of base consumed in titrating 20 mM KCl solutions from pH 3 to 10. Differences in the final solution volumes between the blank and each sample were included in the acidity calculations to normalize titrant consumption.

Collection of UV-vis spectra was accomplished using an Agilent 8453 diode-array spectrophotometer with a 1-cm quartz cuvette. The UV absorbance values at 254, 280, and 365 nm were used to calculate the molar absorptivities at 280 nm (absorbance at 280 nm divided by the C molar concentration) and the E2/E3 ratios (absorbance at 254 nm divided by absorbance at 365 nm) of each sample (Guo and Chorover, 2003).

High performance-size exclusion chromatography was used to estimate the MW_{AP} of the DOM. The system consisted of a Hewlett-Packard (Agilent; San Jose, CA) 1100 high performance liquid chromatography unit equipped with a G1311A quaternary pump, a G1314 auto sampler, and a G1315A photodiode array UV detector. A Waters Protein Pak 125 stainless-steel SEC column with a Waters guard column was used. The mobile phase consisted of a 0.1 M NaCl aqueous solution buffered to pH 6.8 with 5 mM phosphate buffer. Samples were matched to the mobile phase matrix by the addition of 0.1 mL of 1 M NaCl solution (phosphate buffered to pH 6.8) to 0.9 mL of sample. Calibration of molecular weight to retention time was accomplished using polystyrene sulfonate sodium standards (2.0 mg mL⁻¹) of nominal masses of 4.6, 8.0, and 18.0 kDa and polydispersity values of less than 1.2 (Polymer Laboratories; Silver Spring, MD). Benzoic acid and salicylic acid were used as the lowest molecular mass standards in the calibration. The injection volume for all samples was 100 μL and the flow rate was 1.0 mL min⁻¹ with detection at 230 and 254 nm. All standards and samples were analyzed in duplicate.

Dissolved Organic Matter Sorption

A one-point adsorption index with an initial C solution concentration of 5 mM C_{TS} was used to evaluate the extent of

DOM sorption. While precluding an estimation of maximum sorption capacity and bonding affinity, this single-point approach provides relative sorption affinities. Goethite (α -FeOOH) was chosen as the sorbent in this study because of its strong affinity for organic matter, its natural abundance, and its common use in DOM batch sorption studies. In addition, the use of laboratory-synthesized goethite allowed for an examination of the effects of adsorptive fractionation without the potential confounding effects caused by the presence of native mineral C. The goethite was synthesized by using a method modified from Schwertmann and Cornell (1991). Briefly, 13.9 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added to 1 L of DI- H_2O that was de-aerated with N_2 flushing. One hundred and ten mL of 1 M NaHCO_3 solution was then added, and air was bubbled through the reaction vessel at 35 mL min^{-1} for 48 h. The suspension was then centrifuged ($900 \times g$, 30 min). The pellet was retained, washed three times with DI- H_2O , and then dried at 40°C for 24 h. The specific surface area of $58.3 \text{ m}^2 \text{ g}^{-1}$ was determined by triple-point N_2 adsorption.

The adsorption index for each DOM was determined in triplicate by reacting 500 mg of goethite with 30 mL of extract solution containing 5 mM C_{TS} adjusted to pH 6 in 50-mL plastic centrifuge tubes. The tubes were then placed on an orbital shaker at 120 rev min^{-1} for 24 h at 4°C to minimize microbial degradation of the DOM (Zhou and Wong, 2000). No attempt was made to control the pH of the solutions during this time, and pH changes in the DOM were determined at the conclusion of the experiment. The tubes were then centrifuged ($900 \times g$) for 30 min and the supernatants were filtered through $0.40\text{-}\mu\text{m}$ filters. The C_{TS} concentration was determined as described above and the quantity adsorbed was calculated by difference from the initial solution. Post-sorption solutions were also chemically characterized for MW_{AP} and UV absorbance as described above.

Statistical Procedures

Pearson correlation coefficients were generated to examine the relationship between the sorptivity of the DOM and the DOM chemical characteristics of molar absorptivity, MW_{AP} , carboxyl acidity, and phenolic acidity content. Log transformations of the variables were necessary for the data to meet the assumptions of normality (Shapiro-Wilks test) and variance equality (Levene's test). Student t tests were used for determining the statistical significance of the differences between the fresh and decomposed DOM chemical characteristics. Statistical significances were evaluated at $p < 0.05$, $p < 0.01$, and $p < 0.001$ as noted in the text, tables, and figures. All statistical analyses were conducted using the software package SAS 9.1 for Windows.

RESULTS AND DISCUSSION

Dissolved Organic Matter Fractions

The C contents of the HPL and HPB fractions of the extracts before and after decomposition are shown in Fig. 1. The lower DOM content of the soybean and corn shoot biomass as compared to the clover and vetch shoot tissue was likely due to these two materials being collected as field residue after harvest, rather than during an active growth stage. The lower amounts of C in the fresh manure extracts relative to that of the plant extracts may be due to animal metabolic utilization of the more soluble C fractions present in the feed (Merchen, 1988). The total dissolved organic C content of all plant extracts significantly ($p < 0.001$) decreased following

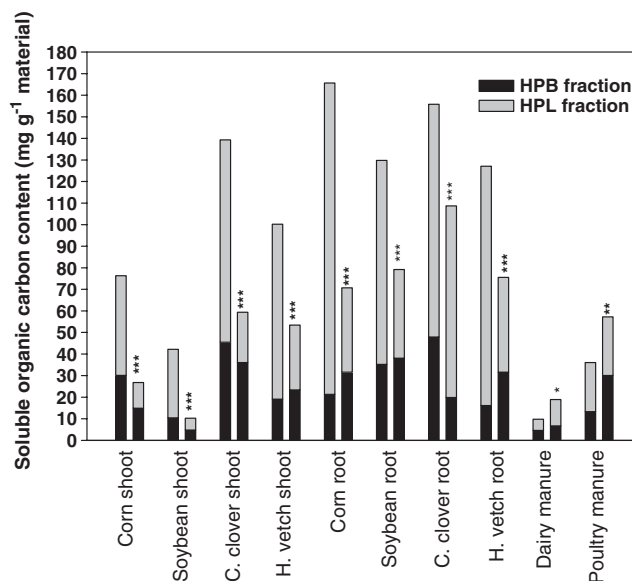


Fig. 1. Water-soluble carbon content of the hydrophilic (HPL) and hydrophobic (HPB) fractions of eight plant and two animal manure residues before incubation (left bar) and after (right bar) a 10-d incubation with microbial inoculation. *, **, and *** designate significant difference between the fresh and decomposed total C content at the $p = 0.05$, 0.01 , and 0.001 levels using the student's t test. NS indicates that the mean difference is not significant.

microbial decomposition. On the other hand, extracts of both animal manures significantly ($p < 0.05$) increased in C content following decomposition. This suggests that the more labile fresh plant material was utilized by microorganisms for energy production and lost as CO_2 , while the more recalcitrant manure material was converted into more water-soluble forms.

The hydrophobicity is operationally defined as the percentage sorbed onto the XAD-7 resin relative to the total C. The mean percentage hydrophobicity for the fresh plant-derived DOM was $24.9 \pm 9.8\%$ as compared to $41.9 \pm 6.4\%$ for the fresh manure-derived DOM. As with the lower DOM content of the manure-derived DOM, the higher mean percentage hydrophobicities of this fraction likely reflect preferential metabolic utilization of the more labile C fraction in the feed. The mean percentage hydrophobicity for the fresh plant material-derived DOM was similar to the value of $\sim 20\%$ found for XAD-8 fractionated early stage compost leachate (Gigliotti et al., 2005) as well as the value of $\sim 30\%$ found for XAD-8/XAD-4 fractionated fresh corn shoot extract (Ohno and Cronan, 1997). Higher percentage hydrophobicity values have typically been found for DOM derived from highly humified materials such as the 72% hydrophobicity value reported for spent mushroom substrate DOM (Guo and Chorover, 2003). Similarly, a study of the humic fraction of DOM from eight European rivers and reservoir waters found hydrophobicity values to range between 41 and 62% (Martin-Mousset et al., 1997).

The mean percentage hydrophobicity values for all plant DOM samples increased following decomposition, from $24.9 \pm 9.8\%$ for the fresh material to $44.8 \pm 14.6\%$ for the decomposed material. This relative increase in

percentage hydrophobicity with decomposition is consistent with the high levels of easily microbially metabolized simple sugars, amino acids, and small chain fatty acids that typically constitute plant biomass extracts. On an individual basis, percentage hydrophobicity significantly ($p < 0.05$) increased for all DOM sources following decomposition, except DOM derived from crimson clover root and dairy cow manure (Fig. 1). The general increase in percentage hydrophobicity observed for the plant DOM samples was primarily due to a relatively larger reduction in the HPL DOM concentration than in the HPB DOM concentration. For manure-derived DOM, C concentrations increased for both HPL and HPB fraction samples and no consistent effect on percentage hydrophobicity was observed.

UV Spectrometry

The increase in percentage hydrophobicity with decomposition was generally supported by the UV absorbance based E2/E3 ratio (Table 1). This ratio has been shown to decrease in value with increasing humification (Guo and Chorover, 2003). For 9 of the 20 DOM samples, the E2/E3 ratio decreased significantly following decomposition, while this ratio increased significantly for only 2 of the samples.

Molar absorptivity at 280 nm has been used extensively as a means of approximating the aromatic content of DOM (Chin et al., 1994; Kalbitz et al., 2003). The mean absorptivity values for both the fresh and decomposed DOM are shown in Table 2. The mean absorptivity of the plant-derived fresh HPL fraction was $14.8 \pm 7.5 \text{ L mol}^{-1} \text{ cm}^{-1}$ while that for the plant-derived fresh HPB fraction was $150 \pm 55 \text{ L mol}^{-1} \text{ cm}^{-1}$, showing the expected preference of the XAD-7 to sorb the more aromatic, more humified plant DOM fraction. Following incubation, the mean absorptivity for the decomposed plant HPL fraction rose significantly to $73.6 \pm 42 \text{ L mol}^{-1} \text{ cm}^{-1}$ while that for the plant HPB fraction did not change significantly ($131 \pm 64 \text{ L mol}^{-1} \text{ cm}^{-1}$). This suggests that the decomposition had a leveling effect on plant DOM properties, generally increasing the aromaticity of the bulk DOM solution.

Table 1. The ratio of ultraviolet absorbance at 250 nm and 365 nm (E2/E3) of the hydrophilic (HPL) and hydrophobic (HPB) fractions of dissolved organic matter (DOM) extracted from plant shoots, roots, and animal manures before and after decomposition.

Material	Fresh DOM		Decomposed DOM	
	HPL fraction	HPB fraction	HPL fraction	HPB fraction
Corn shoot	$9.5 \pm 0.1^\dagger$	3.8 ± 0.2	$1.7 \pm 0.3^{***}$	$1.0 \pm 0.2^{**}$
Soybean shoot	25.7 ± 0.4	3.6 ± 0.2	$2.2 \pm 0.5^{***}$	$2.0 \pm 0.4^*$
Crimson clover shoot	4.8 ± 0.4	2.1 ± 0.1	$11.2 \pm 0.8^{**}$	8.2 ± 0.9
Hairy vetch shoot	5.2 ± 0.3	1.5 ± 0.1	5.7 ± 1.6	1.2 ± 0.9
Corn root	11.4 ± 0.2	4.7 ± 0.4	$5.6 \pm 0.7^{**}$	7.7 ± 1.9
Soybean root	11.0 ± 0.2	8.0 ± 0.1	$1.4 \pm 0.8^{**}$	$3.9 \pm 1.0^*$
Crimson clover root	25.7 ± 0.1	5.5 ± 0.1	29.3 ± 3.0	4.3 ± 2.0
Hairy vetch root	43.5 ± 0.1	13.8 ± 0.2	$3.8 \pm 1.0^{***}$	10.3 ± 1.3
Dairy manure	3.2 ± 0.2	3.7 ± 0.1	1.9 ± 0.8	$2.1 \pm 0.4^*$
Poultry manure	64.0 ± 1.6	6.7 ± 0.1	$6.0 \pm 1.8^{***}$	4.7 ± 2.2

*, **, and *** designate significant difference at the $p = 0.05, 0.01$, and 0.001 levels using the student's t -test between fresh and decomposed means.

† Values are means \pm one standard deviation.

Table 2. The ultraviolet absorptivity at 280 nm of the hydrophilic (HPL) and hydrophobic (HPB) fractions of dissolved organic matter (DOM) extracted from plant shoots, roots, and animal manures before and after decomposition.

Material	Fresh DOM		Decomposed DOM	
	HPL fraction	HPB fraction	HPL fraction	HPB fraction
	$\text{L mol}^{-1} \text{ cm}^{-1}$			
Corn shoot	$23.8 \pm 2.3^\dagger$	202 ± 11	$140 \pm 2.5^{***}$	$120 \pm 5.6^{***}$
Soybean shoot	11.1 ± 0.3	155 ± 1.2	$81.4 \pm 3.2^{***}$	$274 \pm 4.9^{***}$
Crimson clover shoot	15.4 ± 0.1	197 ± 0.5	$25.7 \pm 0.1^{***}$	$100 \pm 1.3^{***}$
Hairy vetch shoot	4.8 ± 0.2	145 ± 0.4	$95.6 \pm 1.0^{***}$	$177 \pm 0.3^{***}$
Corn root	17.9 ± 0.6	210 ± 1.2	$44.8 \pm 7.4^{***}$	$131 \pm 8.4^{***}$
Soybean root	25.6 ± 0.1	101 ± 0.2	$123 \pm 9.0^{***}$	$75.6 \pm 8.1^{**}$
Crimson clover root	4.63 ± 0.3	133 ± 2.7	$56.4 \pm 15.5^{**}$	$91.6 \pm 12.3^{**}$
Hairy vetch root	14.7 ± 0.6	41.6 ± 0.1	$21.8 \pm 4.5^*$	$77.0 \pm 10.3^{**}$
Dairy manure	117 ± 8.5	132 ± 15	$304 \pm 25^{***}$	$392 \pm 2.08^{***}$
Poultry manure	432 ± 0.3	225 ± 0.3	$33.8 \pm 5.9^{***}$	$109 \pm 15.3^{***}$

*, **, and *** designate significant difference at the $p = 0.05, 0.01$, and 0.001 levels using the student's t -test between fresh and decomposed means.

† Values are means \pm one standard deviation.

Absorptivity values for the fresh manure-derived DOM were considerably different from those of the fresh plant-derived DOM. The HPL fractions of the manure-derived DOMs had values for absorptivity that were equal to or considerably greater than those of the corresponding HPB fractions. The much higher mean molar absorptivity value ($432 \text{ L mol}^{-1} \text{ cm}^{-1}$) of the fresh poultry manure-derived HPL fraction relative to that of the fresh HPB fraction may have been due to the presence of high concentrations of relatively polar nitrogen-containing compounds such as polypeptides and nucleic acids in the HPL fraction. Nucleic acids in particular are known to strongly absorb UV radiation in the 260 to 280 nm range and the initial low pH conditions of the XAD technique could have led to their release through microbial lysis. In addition, animal manures are known to contain high concentrations of organic N in the form of both urea and uric acid, the latter of which is an aromatic compound possibly polar enough to pass through the XAD column. Total nitrogen and $\text{NH}_4\text{-N}$ concentrations (data not shown) of the poultry manure-derived HPL fraction decreased from 580 and 486 mg L^{-1} , respectively, to 166 and 54 mg L^{-1} following decomposition. Volatilization of much of this initial NH_4^+ , as well as NH_4^+ produced by mineralization of organic nitrogen, seems likely at the high pH (>9) at which the poultry manure incubation occurred. The low mean molar absorptivity value ($33.8 \pm 5.9 \text{ L mol}^{-1} \text{ cm}^{-1}$) of the decomposed poultry manure-derived HPL fraction and its relatively low sorption to goethite add further evidence to suggest the presence of high amounts of UV absorbing organic N compounds in the fresh poultry manure-derived DOM fraction. The high initial molar absorptivity of the dairy manure-derived HPL DOM may also be due in part to the presence of nitrogenous organic compounds. The high average phenolic acidic content ($4.79 \pm 0.4 \text{ mmol g}^{-1} \text{ C}_{\text{TS}}$) and strong and consistent sorption characteristics of this HPL fraction, as well as its subsequent increase in molar absorptivity following decomposition, however, suggest instead the presence of humified organic carbon compounds. The presence of

high amounts of seemingly humified material in the HPL DOM fraction may have been due to the inability, in this case, of the XAD resin to sorb slightly polar but nonetheless aromatic compounds present in this material.

Nine of the ten total HPL fractions had significantly higher absorptivity values after decomposition, indicating greater aromatic content of the post-decomposition DOM. Following decomposition, four of the ten HPB fractions significantly increased in absorptivity relative to their fresh values, whereas six decreased (Table 2). When the decomposed HPL and HPB fractions are compared, 8 of the 10 highest absorptivity values belong to HPB fractions, as would be expected. It is important to note that the source materials were decomposed and not their extracted DOM solutions. The solutions that were XAD-fractionated before and after decomposition were therefore fundamentally different. The results illustrate the extent and complexity of the changes that can occur to DOM during even a short-term decomposition of its source material. Our results also question the suggestion that the HPB content of all DOM can be easily estimated through UV spectroscopic methods alone (Dilling and Kaiser, 2002). Our results indicate that DOM characteristics are wide ranging, varying greatly within the XAD-separated fractions for different samples and incubation times.

Total and Phenolic Acidity Content

The carboxyl, phenolic, and total acidity content for all of the DOM fractions are shown in Fig. 2. The mean total acidity of the fresh plant-derived HPL fractions was $10.7 \pm 4.0 \text{ mmol g}^{-1} \text{ C}_{\text{TS}}$, whereas that for the manure-derived HPL fraction was $12.9 \pm 4.5 \text{ mmol g}^{-1} \text{ C}_{\text{TS}}$. The fresh HPB fractions of plant- and manure-derived DOM had mean total acidity contents of 9.18 ± 3.3 and $19.7 \pm 3.54 \text{ mmol g}^{-1} \text{ C}_{\text{TS}}$, respectively. Mean phenolic acidity values were greater for both fractions of the fresh manure-derived DOM than for the corresponding fractions of DOM derived from the fresh plant biomass. In addition, mean phenolic acidity values of the plant- and manure-derived HPB DOM fractions were greater than those of the associated HPL fractions. The total acidity for the fresh plant-derived DOM is similar to the value of $12.3 \text{ mmol g}^{-1} \text{ C}_{\text{TS}}$ reported for XAD-8-fractionated HPB DOM derived from forest soils (Vance and David, 1991) as well as the reported value of $12.4 \text{ mmol g}^{-1} \text{ C}_{\text{TS}}$ for a corn HPB fraction sorbed using tandem XAD-4/XAD-8 columns (Ohno and Cronan, 1997). A recent study using whole fraction DOM from similar sources likewise found higher total and phenolic acidity in the animal-derived fraction compared with that derived from plants (Ohno et al., 2006).

Decomposition increased the mean total and phenolic acidity contents of nearly all fractions. The greatest increase in acidity occurred in the plant-derived HPL fraction which increased in both total and phenolic acidity by approximately 40 and 180%, respectively. The manure-derived HPB fraction showed the only decline in mean total acidity, decreasing nearly 35% in value following decomposition. In general, DOM derived from

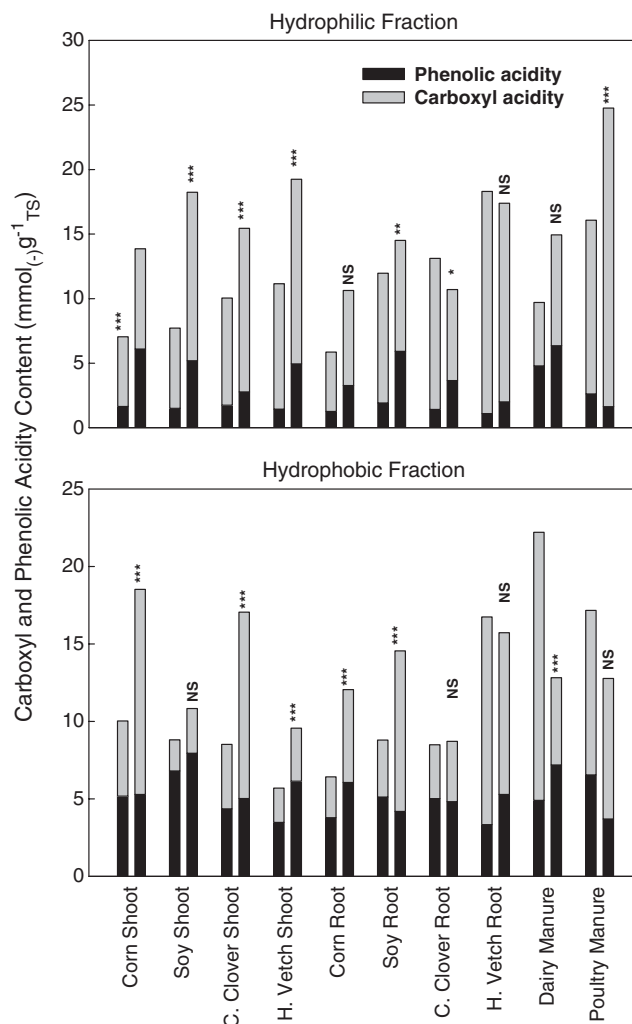


Fig. 2. The carboxyl and phenolic acid content of the hydrophilic and hydrophobic DOM fractions of the plant biomass- and animal manure-derived DOM before (left bar) and after decomposition (right bar). *, **, and * designate significant difference between the fresh and decomposed total acidity content at the $p = 0.05$, 0.01 , and 0.001 levels using the student's t test. NS indicates that the mean difference is not significant.**

plant sources underwent the greatest increases in acidity following decomposition. This increase in acidity content on decomposition of plant biomass supports results from previous studies. A study of early stage humification in agricultural amendments found increases in DOM total charge densities of 166 and 10% in aqueous extracts of wheat straw and crimson clover after 1 wk of incubation (Merritt and Erich, 2003). Evangelou and Marsi (2001) reported an increase exceeding 300% in acidity functional group content for corn shoot extracts following an 8-mo decomposition.

As with other chemical property changes, the general trend of increasing acidity following decomposition likely involves a number of complementary processes. For example, low molecular weight organic acids may form as a result of the incomplete oxidation of labile components. Baziramakenga and Simard (1998) found that aliphatic acids, such as acetic and formic acids, accumulated to concentrations as high as $\sim 123 \text{ mmol kg}^{-1}$

in a variety of manure extracts during the early stages of decomposition. On the other hand, the complete oxidation to CO₂ of labile, nonacidic components such as sugars would lower C_{TS} concentrations and enrich total acidity content as expressed on a C mass basis. Increased DOM structural complexity following the condensation of lower molecular weight compounds to higher molecular weight fulvic acid products represents another process that could generate higher acidic functional group content in DOM (Stevenson, 1994). Spectroscopic proxies should provide clues to the contribution of each of these processes. Phenolic acidity was found to correlate well with absorptivity for the combined decomposed ($r_{adj}^2 = 0.83$) fractions in this study. The general increase in both absorptivity (Table 2) and phenolic acidity (Fig. 2) observed following decomposition of the HPL fraction of plant-derived DOM suggests that a humification process is responsible for the observed increase in the total acidity content of this fraction. Conversely, the lowering of absorptivity and phenolic acidity, along with the simultaneous increase in carboxyl acidity for the poultry manure-derived DOM following decomposition suggests the involvement of incomplete oxidation pathways and the formation of low molecular weight organic acids.

Apparent Molecular Weight

The range of MW_{AP} for all of the fresh and decomposed DOMs in this study was 209 to 13000 Da. The MW_{AP} values for the HPB fraction, or "humic fraction," alone ranged between 242 and 4100 Da. Typical values for aquatic and terrestrial humic substances have been found by HPSEC to be ~1800 for Suwannee River fulvic acid (Wang et al., 1997) and ~7000 to ~20000 for humic and fulvic acids extracted from soil, peat, lignite, and lake water (Balcke et al., 2002). The fresh HPL and HPB fractions were generally of relatively low MW_{AP}, under 700 Da. The only exceptions to this were the MW_{AP} values of the soybean shoot-derived HPB fraction and both fractions of the dairy manure-derived DOM, which ranged between 2350 and 9040 Da. The MW_{AP} of all fresh DOM increased on decomposition, with the mean value increasing from 1020 to 2860 Da. The largest increase in MW_{AP} was found for the plant-derived HPL fraction where the mean MW_{AP} value increased by an order of magnitude from 300 to 3310 Da (Table 3). The increase in MW_{AP} was less pronounced for the plant-derived HPB DOM with a mean increase in MW_{AP} of 70% (584 to 994 Da). The MW_{AP} of the dairy manure-derived DOM was much higher than that of the poultry manure-derived DOM in both the fresh HPL and fresh HPB fractions. Following decomposition, the mean MW_{AP} of the dairy manure-derived HPL and HPB fractions increased 44 and 24% respectively, whereas the mean MW_{AP} of poultry manure-derived HPL and HPB fractions increased 1500 and 70%, respectively. The MW_{AP} was not found to correlate well with either absorptivity or phenolic acidity in any of the fractions.

Accurate molecular mass determination with high performance-size exclusion chromatography requires that the transport of components through the column be based

Table 3. The apparent molecular weight (MW_{AP}) of the hydrophilic (HPL) and hydrophobic (HPB) fractions of dissolved organic matter (DOM) extracted from plant shoots, roots, and animal manures before and after sorption to goethite.

Material	Fresh DOM		Decomposed DOM	
	Pre-sorption	Post-sorption	Pre-sorption	Post-sorption
	Da			
HPL Fraction				
Corn shoot	514 ± 7†	311 ± 12	5370 ± 330***	178 ± 14
Soybean shoot	466 ± 9	219 ± 27	6740 ± 628***	234 ± 32
Crimson clover shoot	209 ± 9	161 ± 22	5950 ± 238***	190 ± 8
Hairy vetch shoot	227 ± 10	212 ± 12	2320 ± 350***	223 ± 44
Corn root	321 ± 11	132 ± 21	983 ± 189**	315 ± 5
Soybean root	222 ± 11	179 ± 9	2990 ± 115***	215 ± 17
Crimson clover root	215 ± 5	171 ± 23	1290 ± 100***	288 ± 29
Hairy vetch root	209 ± 6	138 ± 8	892 ± 62***	155 ± 23
Dairy manure	9040 ± 219	326 ± 18	13000 ± 460***	217 ± 10
Poultry manure	267 ± 15	225 ± 11	4280 ± 215***	248 ± 17
HPB Fraction				
Corn shoot	605 ± 11	237 ± 30	907 ± 223*	192 ± 31
Soybean shoot	2350 ± 29	361 ± 43	2750 ± 399	289 ± 16
Crimson clover shoot	258 ± 13	173 ± 16	699 ± 33***	226 ± 22
Hairy vetch shoot	242 ± 5	186 ± 14	884 ± 189**	239 ± 11
Corn root	380 ± 9	169 ± 11	676 ± 53***	288 ± 16
Soybean root	292 ± 9	247 ± 8	655 ± 53***	253 ± 54
Crimson clover root	277 ± 12	229 ± 9	588 ± 94**	289 ± 32
Hairy vetch root	278 ± 11	175 ± 6	752 ± 26***	208 ± 8
Dairy manure	3300 ± 58	246 ± 14	4100 ± 25***	207 ± 2
Poultry manure	675 ± 25	244 ± 6	1150 ± 187***	298 ± 2

*, **, and *** designate significant difference at the $p = 0.05$, 0.01 , and 0.001 levels using the student's t -test between fresh and decomposed means. † Values are means ± one standard deviation.

entirely on differences in their hydrodynamic sizes and not by electrostatic or other "non-size exclusion" effects and also that response of the detector adequately reflect mass frequency. However, highly charged, very low molecular weight organic acids may be electrostatically influenced despite a high ionic strength mobile phase. In addition, UV absorbance in the 230 to 254 nm range is proficient only at detecting C compounds possessing extensive π electron systems such as those present in conjugated dienes or aromatic functional groups. Thus the proportionality between UV absorbance and mass frequency may be an inappropriate assumption when working with C compounds lacking strong aromatic chromophores, such as nonhumic compounds with aliphatic dominated structures. The application of size-exclusion chromatography with UV detection may therefore give misleading results because a significant fraction of the DOM may not be included in the resultant MW_{AP} calculation. Some of the DOM extracts are in the category of nonhumic, low aromatic content materials; thus the absolute molecular weights given in this article should be interpreted with caution. It is only correct to view these MW_{AP} values as being representative of the chromophores within each extract. Without the use of a total organic C detector capable of detecting all forms of organic C in the samples, the magnitude of this second source of error is undeterminable. As a gauge of the effects of both decomposition and sorption on DOM chromophores, however, this method provides valuable information.

Sorption to Goethite

The quantities of DOM sorbed in units of $\mu\text{g C m}^{-2}$ onto goethite at the single point initial concentration of

5 mM C_{TS} for the HPL and HPB fractions are shown in Fig. 3. Division by 0.6 of the sorbed quantity (in $\mu\text{g C m}^{-2}$) gives an estimate of the percentage sorbed. For the fresh plant-derived DOM, the HPB fraction sorbed to goethite to a greater extent than did the HPL fraction, with mean sorbed amounts of 28.0 ± 9.4 ($\sim 47\%$) and $16.4 \pm 5.7 \mu\text{g C m}^{-2}$ ($\sim 27\%$), respectively. Both fractions of fresh dairy manure-derived DOM sorbed similarly and exhibited the greatest affinity for goethite ($>90\%$ sorbed) of all the DOM materials. The two fresh poultry manure-derived DOM fractions behaved similarly to the plant-derived DOM, with the HPB fraction sorbing to a greater extent ($36.4 \pm 0.4 \mu\text{g C m}^{-2}$) than the HPL fraction ($24 \pm 0.3 \mu\text{g C m}^{-2}$).

Decomposition increased the sorptivity of both the HPL and HPB fractions of the plant-derived DOM (Fig. 3). In contrast, decomposition decreased or did not affect the sorptivity for the two manure-derived DOMs. This difference in the effect of decomposition on sorption again emphasizes the differences in chemical be-

havior and properties between the DOM derived from plant and animal manure sources. A C mass balance calculation determined that the overall amount of C sorbed per gram of original residue increased overall for 6 out of the 10 materials used. The DOM derived from soybean shoot, cow manure, and all of the root samples sorbed more C to goethite following decomposition than before. In most cases this additional sorption was due to both the simultaneous relative or absolute concentration increase in the stronger sorbing HPB fraction and to an overall increase in the sorptivity of both the HPL and HPB fractions. The crimson clover root-derived HPB fraction underwent a relative decrease in concentration following decomposition, thus the overall additional sorption observed for crimson clover root DOM arose entirely from the increased sorptivity of its HPL fraction. A decrease in the overall C sorption was observed with DOM derived from poultry manure residue and the shoots of crimson clover, hairy vetch, and corn. For these plant-derived DOM samples, the increased sorptivity of the decomposed extracts did not compensate for their concurrent overall loss in C concentration. As stated earlier, the sorptivity of poultry manure-derived DOM decreased following decomposition. Thus, the increased C concentrations of the poultry manure-derived DOM fractions following decomposition did not offset the decreased sorptivity of these fractions.

Correlation analyses were performed on some of the major sample groupings to relate the observed sorption (Fig. 3) to the experimentally determined MW_{AP} and absorptivity, carboxyl acidity, and phenolic acidity values (Table 4). For all major sample groupings phenolic acidity content was much better correlated to DOM sorption than was carboxyl acidity content. This is consistent with results reported by Davis (1982), who observed preferential sorption onto aluminum oxides of acids having higher pK_a values as compared with those possessing greater acidity. At the experimental pH of 6 used in this sorption study, organic acids with low pK_a values would be expected to be primarily dissociated and therefore less available to protonate potential Lewis acid sites on the goethite surface. Phenolic acidity content was more strongly correlated to the sorption of the HPL DOM fraction than to that of the HPB DOM fraction, suggesting that ligand exchange played a more important role in the sorption of the HPL DOM to goethite. Following decomposition, the correlation between DOM sorption and absorptivity increased, while the correlation between sorption and phenolic acidity content did not change appreciably. This implies that the enhanced sorption observed in most cases following decomposition can be attributed to hydrophobic effects that complement the primary mechanism of ligand exchange. Molar absorptivity was generally well correlated to the operationally defined phenolic acid content, indicating that the compounds responsible for this acidity were considerably aromatic in nature.

The preference for sorption of the higher molecular weight DOM fraction is evident in the post-sorption MW_{AP} values of the supernatant solutions as shown in Table 3. The MW_{AP} range for the solutions before sorption was 209 to 13000 Da, whereas that following sorp-

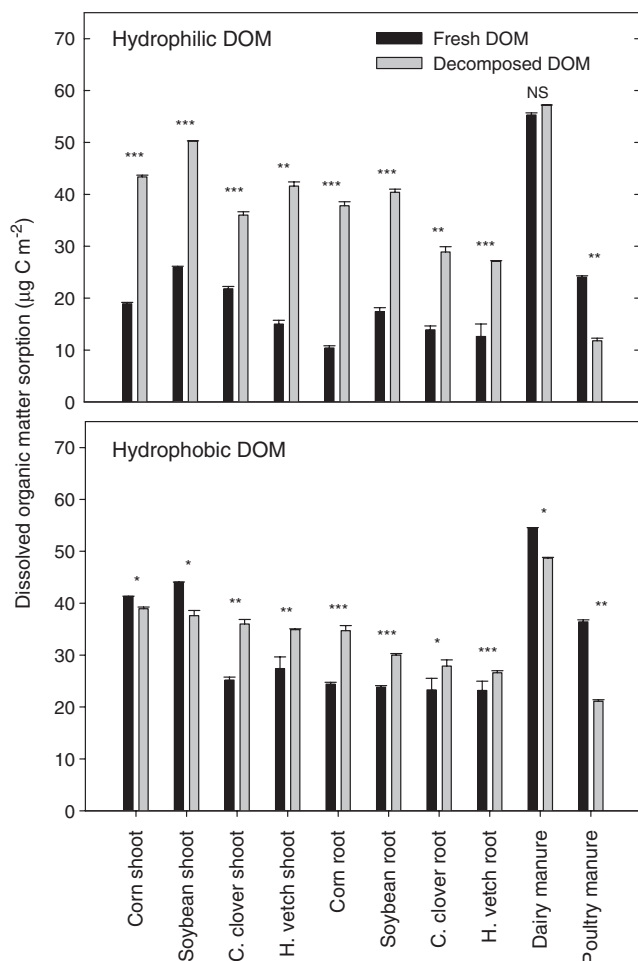


Fig. 3. The sorption onto goethite of 60 mg C L⁻¹ solutions of the hydrophilic and hydrophobic DOM fractions of the plant biomass- and animal manure-derived DOM before and after decomposition. Error bars indicate standard deviation of the mean of three replicates. *, **, and *** designate significant difference at the $p = 0.05$, 0.01 , and 0.001 levels using the student's t test between the fresh and decomposed means. NS indicates that the mean difference is not significant.

Table 4. Correlation coefficients relating sorption characteristics to the log transformed values of the chemical properties of five groupings of dissolved organic matter extracted from animal manures and plant biomass.

Grouping	Variables	Sorption	MW _{AP}	Molar absorption	Carboxyl acidity	Phenolic acidity
Total	MW _{AP}	0.084***	1.000	–	–	–
	Absorptivity	0.620***	0.383***	1.000	–	–
	Carboxyl acidity	–0.059 ^{NS} †	0.150 ^{NS}	–0.313 ^{NS}	1.000	–
	Phenolic acidity	0.732***	0.501***	0.839***	–0.274**	1.000
Fresh HPL	MW _{AP}	0.318 ^{NS}	1.000	–	–	–
	Absorptivity	0.119 ^{NS}	0.215 ^{NS}	1.000	–	–
	Carboxyl acidity	–0.668***	0.635***	–0.002 ^{NS}	1.000	–
	Phenolic acidity	0.897***	0.515**	0.227 ^{NS}	0.744***	1.000
Decomp. HPL	MW _{AP}	0.575***	1.000	–	–	–
	Absorptivity	0.770***	0.600***	1.000	–	–
	Carboxyl acidity	–0.401**	0.055 ^{NS}	–0.426*	1.000	–
	Phenolic acidity	0.830***	0.475**	0.860***	–0.484*	1.000
Fresh HPB	MW _{AP}	0.907***	1.000	–	–	–
	Absorptivity	0.423*	0.172 ^{NS}	1.000	–	–
	Carboxyl acidity	0.233 ^{NS}	0.286 ^{NS}	–0.369*	1.000	–
	Phenolic acidity	0.578***	0.554**	0.436*	–0.008 ^{NS}	1.000
Decomp. HPB	MW _{AP}	0.657***	1.000	–	–	–
	Absorptivity	0.797***	0.879***	1.000	–	–
	Carboxyl acidity	–0.117 ^{NS}	–0.144 ^{NS}	–0.394*	1.000	–
	Phenolic acidity	0.606**	0.728***	0.869***	–0.376*	1.000

*, **, and *** designate significant difference at the $p = 0.05$, 0.01 , and 0.001 levels.

†NS, not significant.

tion was a narrow 138 to 361 Da (Table 3). Sorptive fractionation has been reported for humic substances extracted from aquatic and terrestrial sources (Jardine et al., 1989; Wang et al., 1997; Chorover and Amistadi, 2001; Hur and Schlautman, 2004) and this study demonstrates that water-extracted organic matter from plant biomass and animal manures are also subject to molecular weight fractionation due to the preferential sorption of the higher molecular weight fraction.

CONCLUSIONS

The objectives of this study were to determine the effect of decomposition on the chemical properties of water-extractable HPL and HPB fractions of DOM derived from plant biomass and animal manures, as well as to assess the relationship of these parameters to sorption onto goethite. This research was designed to ultimately increase our understanding of soil organic C pools through the elucidation of processes affecting DOM characteristics and distributions. Incorporation of crop biomass and animal manures is common in sustainable agricultural systems to increase both soil quality and plant nutrient bioavailability. Our results show that for the majority of sources, DOM sorption generally increased after decomposition due to the increased sorptivity of both the decomposed HPL and HPB fractions. While the eight sources of plant biomass and the two animal manures may not represent the entire family of C-rich materials that are used as soil amendments, they do represent amendments used very commonly in U.S. agriculture. This study also shows the strong preferential sorption of the high molecular weight DOM components to goethite for all HPL and HPB fractions investigated. The results of our study have implications for both the maintenance of soil quality and nutrient availability. The data suggests that amendment with plant biomass and animal manures that release DOM of higher molecular weight, greater aromaticity, and phenolic acidity will result in enhanced initial sorption to

mineral soil surfaces. This work also demonstrated that in contrast to previously-published observations, DOM characteristics were wide-ranging, varying greatly within fractions for different samples and incubation times. Furthermore, microbially-driven decomposition processes resulted in greater sorption of plant- and manure-derived DOM to soil solid components.

ACKNOWLEDGMENTS

This project was supported by National Research Initiative Competitive Grant no. 2003-35107-13628 from the USDA Cooperative State Research, Education, and Extension Service. This study has also been supported by Hatch funds provided by the Maine Agricultural and Forest Experiment Station. This is MAFES Journal Publication No. 2884.

REFERENCES

- Aoyama, M. 1996. Use of high performance size exclusion chromatography to monitor the dynamics of water-soluble organic substances during the decomposition of plant residues in soil. *Soil Sci. Plant Nutr.* 42:21–30.
- Balcke, G.U., N.A. Kulikova, S. Hesse, F.D. Kopinke, I.V. Perminova, and F.H. Frimmel. 2002. Adsorption of humic substances onto kaolin clay related to their structural features. *Soil Sci. Soc. Am. J.* 66:1805–1812.
- Baziramakenga, R., and R.R. Simard. 1998. Low molecular weight aliphatic acid contents of composted manures. *J. Environ. Qual.* 27: 557–561.
- Chin, Y.P., G. Aiken, and E. O’Laughlin. 1994. Molecular weight, polydispersity and spectroscopic properties of aquatic humic substances. *Environ. Sci. Technol.* 28:1853–1858.
- Chorover, J., and M.K. Amistadi. 2001. Reaction of forest floor organic matter at goethite, birnessite and smectite surfaces. *Geochim. Cosmochim. Acta* 65:95–109.
- Davis, J.A. 1982. Adsorption of natural dissolved organic matter at the oxide/water interface. *Geochim. Cosmochim. Acta* 46: 2381–2393.
- Dilling, J., and K. Kaiser. 2002. Estimation of the hydrophobic fraction of dissolved organic matter in water samples using UV photometry. *Water Res.* 36:5037–5044.
- Evangelou, V.P., and M. Marsi. 2001. Composition and metal ion complexation behavior of humic fractions derived from corn tissue. *Plant Soil* 229:13–24.
- Gadmar, T.C., R.D. Vogt, and L. Evje. 2005. Artifacts in XAD-8 NOM fractionation. *Int. J. Environ. Anal. Chem.* 85:365–376.

- Gigliotti, G., F.G. Erriquens, and D. Said-Pullicino. 2005. Changes in the chemical characteristics of dissolved organic matter during the composting process and their influence on compost stability and maturity. *GeoPhys. Res. Abs.* 7:02416, SRef-ID: 1607-7962/gr/EGU05-A-02416.
- Griffin, T.S., and G. Porter. 2004. Altering soil carbon and nitrogen stocks in intensively tilled two-year rotations. *Biol. Fertil. Soils* 39: 366-374.
- Gu, B., J. Schmitt, Z. Chen, L. Liang, and J.F. McCarthy. 1995. Adsorption and desorption of different organic matter fractions on iron oxide. *Geochim. Cosmochim. Acta* 59:219-229.
- Guo, M., and J. Chorover. 2003. Transport and fractionation of dissolved organic matter in soil columns. *Soil Sci.* 168:108-118.
- Hur, J., and M. Schlautman. 2003. Molecular weight fractionation of humic substances by adsorption onto minerals. *J. Coll. Int. Sci.* 264:313-321.
- Hur, J., and M.A. Schlautman. 2004. Effects of pH and phosphate on the adsorptive fractionation of purified Aldrich humic acid on kaolinite and hematite. *J. Coll. Int. Sci.* 277:264-270.
- Jardine, P.H., N.L. Weber, and J.F. McCarthy. 1989. Mechanisms of organic carbon adsorption on soil. *Soil Sci. Soc. Am. J.* 53: 1378-1385.
- Kaiser, K., and W. Zech. 1997. Competitive sorption of dissolved organic matter fractions to soils and related mineral phases. *Soil Sci. Soc. Am. J.* 61:64-69.
- Kaiser, K., and G. Guggenberger. 2000. The role of dissolved organic matter sorption to mineral surfaces in the preservation of organic matter in soils. *Org. Geochem.* 31:711-725.
- Kalbitz, K., J. Schmerwitz, D. Schwesig, and E. Matzner. 2003. Biodegradation of soil-derived dissolved organic matter as related to its properties. *Geoderma* 113:273-291.
- Marschner, B., and R. Bredow. 2002. Temperature effects on release and ecologically relevant properties of dissolved organic carbon in sterilized and biologically active soils. *Soil Biol. Biochem.* 33: 805-813.
- Marschner, B., and K. Kalbitz. 2003. Controls of bioavailability and biodegradability of dissolved organic matter in soils. *Geoderma* 113:211-235.
- Martin-Mousset, B., J.P. Croue, E. Lefebvre, and B. Lgube. 1997. Distribution and characterization of DOM of surface waters. *Water Res.* 31:541-553.
- Meier, M., K. Namjesnik-Dejanovic, P. Maurice, Y.P. Chin, and G. Aiken. 1999. Fractionation of aquatic natural organic matter upon sorption to goethite and kaolinite. *Chem. Geol.* 157:275-284.
- Merchen, N.R. 1988. Digestion, absorption, and excretion in ruminants. p. 172-201. *In* D.C. Church (ed.) *The ruminant animal: Digestive physiology and nutrition*. Waveland Press, Prospect Heights, IL.
- Merritt, K.A., and M.S. Erich. 2003. Influence of organic matter decomposition on soluble carbon and its copper binding capacity. *J. Environ. Qual.* 32:2122-2131.
- Morel, F., and J.G. Hering. 1993. *Principles and applications of aquatic chemistry*. John Wiley & Sons, New York.
- Ohno, T., J. Chorover, A. Omoike, and J. Hunt. 2006. Molecular weight and humification index as a predictor of plant and animal manure-derived dissolved organic matter to goethite. *Eur. J. Soil Sci.* (in press).
- Ohno, T., and C.S. Cronan. 1997. Comparative effects of ionic and nonionic resin purification treatments on the chemistry of dissolved organic matter. *Int. J. Environ. Anal. Chem.* 66:119-136.
- Ohno, T., T.S. Griffin, M. Liebman, and G.A. Porter. 2005. Green and animal manure-based cropping systems effects on soil phosphorus and organic matter. *Agric. Ecosyst. Environ.* 105:625-634.
- Schwertmann, U., and P. Cornell. 1991. *Iron oxides in the laboratory: Preparation and characterization*. VCH, New York.
- Sposito, G. 1989. *The chemistry of soils*. Oxford Univ. Press, New York.
- Stevenson, F.J. 1994. *Humus chemistry: Genesis, composition, reactions*. 2nd ed. John Wiley & Sons, New York.
- Vance, G.F., and M.B. David. 1991. Chemical characteristics and acidity of soluble organic substances from a northern hardwood forest floor, central Maine, USA. *Geochim. Cosmochim. Acta* 55: 3611-3625.
- Wang, L.L., Y.-P. Chin, and S.J. Traina. 1997. Adsorption of (poly)-maleic acid and an aquatic fulvic acid by goethite. *Geochim. Cosmochim. Acta* 61:5313-5324.
- Zhaoyi, X., Z. Quanxing, W. Changlong, and W. Liansheng. 1997. Adsorption of naphthalene derivatives on different macroporous polymeric adsorbents. *Chemosphere* 35:2269-2276.
- Zhou, L.X., and J.W.C. Wong. 2000. Microbial decomposition of dissolved organic matter and its control during a sorption experiment. *J. Environ. Qual.* 29:1852-1856.
- Zhou, Q., S.E. Cabaniss, and P. Maurice. 2000. Considerations in the use of high-pressure size exclusion chromatography (HPSEC) for determining molecular weights of aquatic humic substances. *Water Res.* 34:3505-3514.